Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

# Table of Contents

## 1. Methods

Electrospray Ionisation Mass Spectrometry: ESI-MS measurements were performed on an AB SciEX Triple TOF 4600 spectrometer operating in negative mode. All samples were prepared to a concentration of 5 x $10^{-6}$ M in acetonitrile and introduced by direct injection via an integrated syringe pump at a constant flow rate of 5 µL $min^{-1}$. Source parameters were as follows: source voltage: 5.5 kV, source temperature: 150 °C, de-clustering potential: 25 V, collision energy: 10 V.

Mass spectra of the organic compounds were recorded on a Bruker MicroTOF spectrometer ionised by electrospray ionisation (ESI).

UV-vis spectroscopy of all samples was performed on a PerkinElmer Lambda 25 UV/Vis Spectrophotometer.

Infra-red spectra were measured using a Bruker Alpha FTIR spectrometer with a platinum ATR module.

$^1$H NMR- and $^{31}$P NMR-spectra were obtained using a Bruker DPX 300 and a Bruker AV3400 spectrometer.

CHN microanalysis was carried out using a CE-440 Elemental Analyser by Exeter Analytical.

ICP-OES data were recorded on a PerkinElmer Optima 2000 Optical Emission Spectrometer.

Thermogravimetric analysis was employed with a TA-Q500 (TA Instruments), samples were heated from 25-1000°C under inert atmosphere at 10°C/min.

HRTEM imaging was performed using a JEOL 2100F transmission field electron microscope (field emission gun source, information limit 0.19 nm) operating at an accelerating voltage of 200 kV. TEM samples were prepared by casting several drops of a sample solution onto copper-mesh TEM grid mounted with a holey carbon film and dried under standard conditions unless stated otherwise.

Dynamic Light Scattering (DLS) and Zeta-potential measurements were acquired using a Malvern Instrument Nano-ZS Zetasizer at room temperature.

Electrochemical measurements were performed on a CHI600e (CH Instruments) workstation.

## 2. Syntheses and Materials

All reagents were obtained from commercial sources and were used without further purification. The precursors $K_6[P_2W_{18}O_{62}]$ and $K_{10}[P_2W_{17}O_{61}]$ were prepared by reported methods. [1]

***Synthesis of (11-bromoundecyl)ethanethioate (A)***

Under argon atmosphere, 11-Bromo-1-undecene (3 ml, 3.2 g, 13.0 mmol, 1.0 eq) was added to dry toluene (40 ml). After the careful addition of thioacetic acid (3.6 ml, 3.8 g, 48.3 mmol, 3.7 eq) the reaction mixture was heated to 55°C. Freshly recrystallized 2,2'-Azobis(2-methylproprionitrile) (AIBN) (1 g, 6.1 mmol, 0.5 eq) was then added and the solution was heated to 80°C for 4h. After cooling the reaction mixture to room temperature, the toluene layer was washed with saturated $NaHCO_3$ solution (3 x 40 ml) and deionized water (40 ml). The organic layer was then dried over $MgSO_4$. Toluene was then removed in vacuo and the residue was then further purified via silica column chromatography (petroleumether/ethylacetate, v/v = 70/1) yielding a yellow oil.

Yield: 3.84 g (12.4 mmol, 96 %)
δH (300 MHz, $CDCl_3$) 3.38 (t, 2H, **$CH_2$**, J = 6.9 Hz), 2.84 (t, 2H, **$CH_2$**, J = 7.3 Hz), 2.29 (s, 3H, **$CH_3$**), 1.83 (m, 2H, **$CH_2$**), 1.45 – 1.21 (m, 16H, **$CH_2$**).

***Synthesis of (11-(4-bromophenoxy)undecyl)ethanethioate (B)***

**A** (2g, 6.5 mmol, 1.0 eq) and 4-Bromophenol (1.45 g, 8.4 mmol, 1.3 eq) were dissolved in 16 ml *N,N'*-dimethylformamide. To this solution potassium iodide (0.200 g, 1.2 mmol) and potassium carbonate (3.50 g, 25.3 mmol) were added. The reaction mixture was heated to 60°C for 20h. After the solvent had been removed in vacuo, a mixture of diethylether (15 ml) and 2N NaOH (10 ml) were added. The aqueous layer was washed two more times with diethylether (15 ml). The combined organic layers were washed with 2N NaOH (3 x 15 ml) and brine (15 ml). The diethyl ether layer was dried over $MgSO_4$. The solvent was removed *in vacuo* yielding a yellow solid.

Yield: 1.87 g (4.7 mmol, 72 %)
δH (400 MHz, $CDCl_3$) 7.41 – 7.33 (m, 2H, **CH**), 6.81 – 6.72 (m, 2H, **CH**), 3.92 (t, 2H, **$CH_2$**, *J* = 6.5 Hz), 2.87 (t, 2H, **$CH_2$**, *J* = 7.3 Hz), 2.31 (s, 3H, **$CH_3$**), 1.81 – 1.74 (m, 2H, **$CH_2$**), 1.40 – 1.25 (m, 16H, **$CH_2$**).
ESI-MS (+ ve): m/z = 423.1 (calculated: m/z = 423.1)

***Synthesis of (11-(4-(diethoxyphosphoryl)phenoxy)undecyl)ethanethioate (C)***

In a microwave tube under argon atmosphere **B** (0.5 g, 1.5 mmol, 1eq) was added to a mixture of triethylphosphite (0.50 ml, 2.9 mmol, 1.9 eq) and anhydrous NiCl (0.05 g, 0.38 mmol, 0.3eq). The mixture was heated under microwave conditions at 160 °C for 4h.
The dark reaction mixture was poured into diethylether. The black precipitate was filtered off and the solvent was reduced from the filtrate in vacuo. The pure product was obtained as a pale yellow oil after silica column chromatography (chloroform/ethylacetate v/v = 3/1) and removal of solvent *in vacuo*.
Y: 0.25 g (0.5 mmol, 36 %)
ESI-MS (+ ve): m/z = 481.2 (calculated: m/z = 481.2)

### *Synthesis of (4-((11-(acetylthio)undecyl)oxy)phenyl)phosphonic acid (D)*

Under argon atmosphere, **C** (1.00 g, 2.2 mmol, 1eq) was dissolved in 15 ml dry dichloromethane. After addition of bromotrimethylsilane (1.4 ml, 1.6 g, 10.3 mmol, 4.7 eq) the reaction mixture was stirred for 20h at room temperature. The solvent was removed *in vacuo* yielding a pale yellow-green oil. A solvent mixture of 12 ml of MeOH/DCM (v:v = 1:1) was added and the solvent was again removed in vacuo. The resulting faint yellow solid was recrystallised from diethyl ether and pentane to give a white powder.

Yield: 0.41 g (1.0 mmol, 47 %)
δH (300 MHz, $C_2D_6OS$) 7.63 – 7.54 (m, 2H, **CH**), 6.97 (m, 2H, **CH**), 3.99 (d, 2H, **$CH_2$**, J = 13.0 Hz), 2.82 (t, 2H, **$CH_2$**, J = 7.2 Hz), 2.57 – 2.42 (m, 4H), 2.31 (s, 3H, **$CH_3$**), 1.78 – 1.62 (m, 2H, **$CH_2$**), 1.55 – 1.20 (m, 16H, **$CH_2$**).
δP (121 MHz, $C_2D_6OS$) 13.53.
ESI-MS (- ve): m/z = 401.2 (calculated: m/z = 401.2)
Characteristic IR bands ($cm^{-1}$): 1690 (m), 1598 (m), 1569 (w), 1506 (w), 1469 (w), 1444 (w), 1409 (w), 1396 (w), 1294 (w), 1241 (m), 1179 (w), 1165 (w), 1134 (m), 1108 (w), 1099 (w), 1021 (m), 958 (m), 831 (w), 794 (m), 753 (w), 722 (w), 679 (w), 662 (w), 625 (m), 564 (m), 539 (m).

### *Synthesis of $H_6[P_2W_{17}O_{57}(C_{17}H_{27}O_4PS)_2]\cdot 4C_4H_9NO$ ($H_6$1)*

**D** (0.15 g, 0.37 mmol, 2.1 eq) and $K_{10}P_2W_{17}O_{61}$ (0.8 g, 0.17 mmol, 1 eq) [1] were suspended in 24 ml *N*,*N*-dimethylacetamide and 80 ml HCl (37 wt-%). The reaction mixture was stirred at 75 °C for 72h. The resulting brown precipitate was filtered off and washed several times with cold water and ethanol then sonicated in diethyl ether to remove unreacted ligand. The brown solid was dried under high vacuum at 70 °C overnight.

Yield: 0.3 g (0.06mmol) (34 % based on W).
δH (400 MHz, $C_3D_7NO$) 8.29 (dd, 4H, **CH**, *J* = 13.4, 8.3 Hz), 7.24 (dd, 4H, **CH**, *J* = 8.8, 3.3 Hz), 4.33 – 4.22 (m, 4H, **$CH_2$**), 1.98 (p, *J* = 6.5 Hz, 4H, **$CH_2$**), 1.81 – 1.45 (m, 34H, **$CH_2$**, **SH**).
δP (162 MHz, $C_3D_7NO$) 16.08, -10.74, -12.35.
Elemental analysis for $C_{50}H_{96}S_2P_4W_{17}O_{69}N_4$ in wt% (calcd.): C: 11.35 (11.64), H: 1.84 (1.87), N: 0.69 (1.08), W: 60.60 (60.44).
Characteristic IR bands ($cm^{-1}$): 1596-1567 (m), 1504 (m), 1460-1438 (m), 1409 (w), 1311-1292 (w), 1253 (m), 1132 (m), 1085 (s), 1050 (m), 1017 (m), 954 (s), 905 (s), 798,765, 716, 613 (vs), 588-566 (s), 523 (s), 471 (s), 422 (m).

## 3. FTIR Analysis

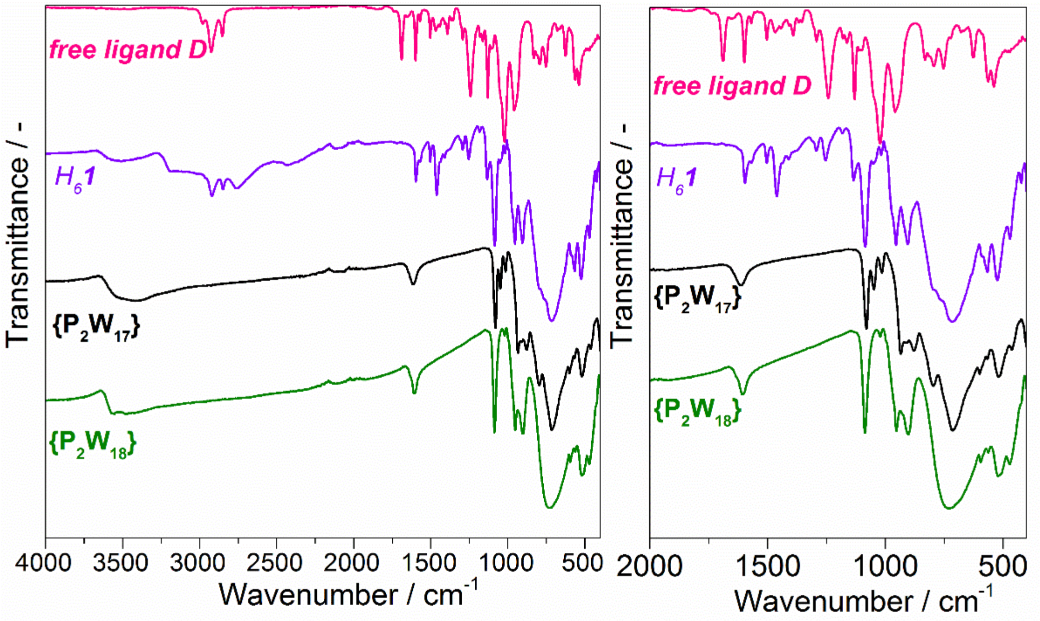

*Figure S1 Comparison of ATR IR spectra of* $H_6$***1*** *(violet)****,*** *the organophosphonate ligand* ***D*** *(pink), the non-functionalised lacunary parent-anion* $[P_2W_{17}O_{61}]^{10-}$ *=* $\{P_2W_{17}\}$ *(black) and the polyoxometalate precursor* $[P_2W_{18}O_{62}]^{6-}$ *=* $\{P_2W_{18}\}$ *(green).*

## 4. NMR characterisation

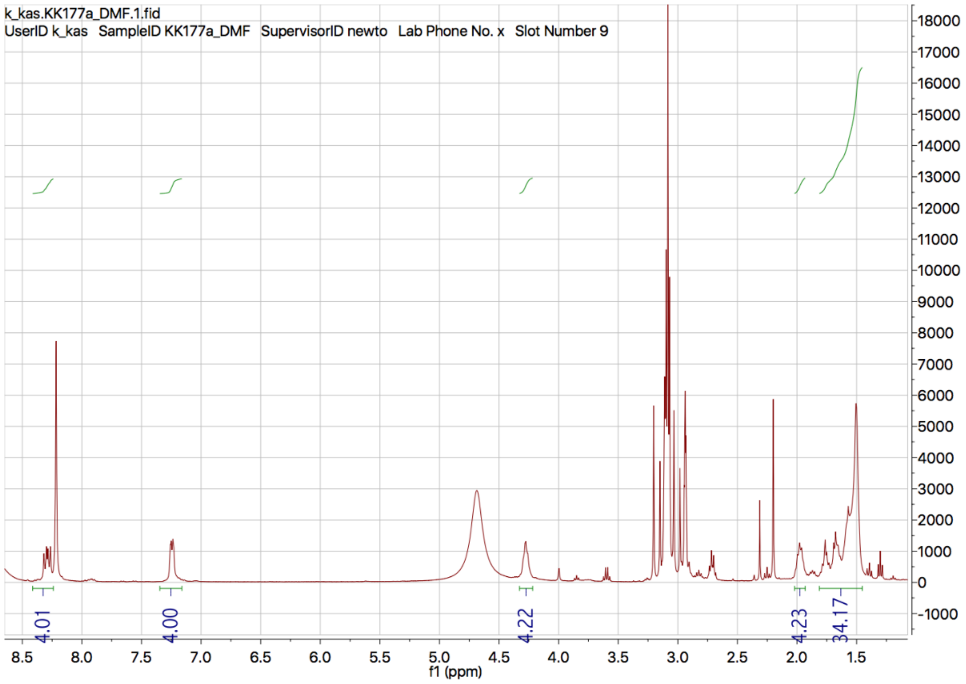

*Figure S2 $^1$H-NMR of $H_6\mathbf{1}$ in DMF-$d_7$.*

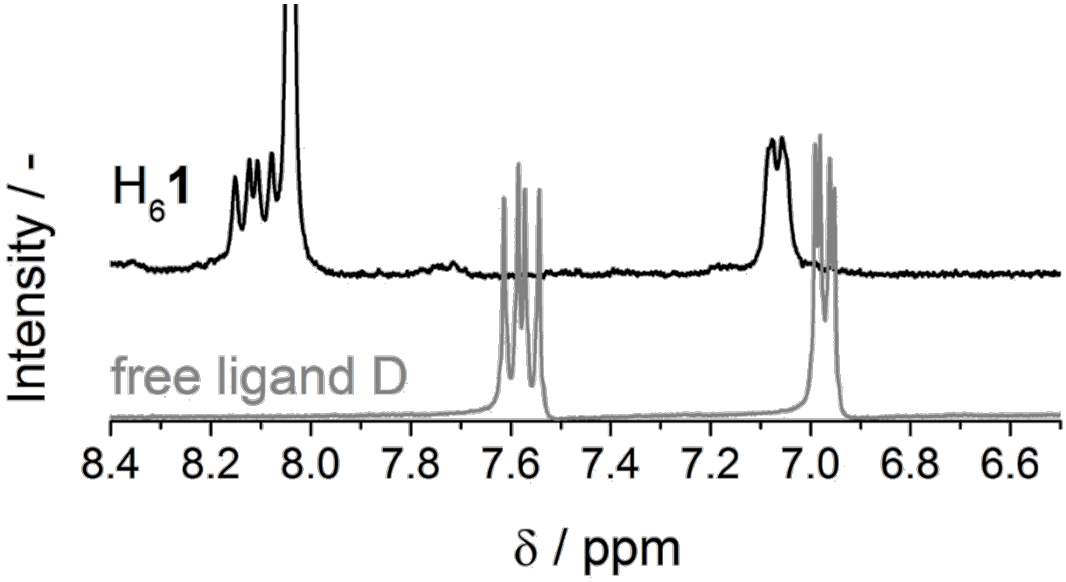

*Figure S3. Comparison of the aromatic regions in the $^1$H-NMR spectra of $H_6\mathbf{1}$ and the free ligand 'D' in DMSO-$d_6$.*

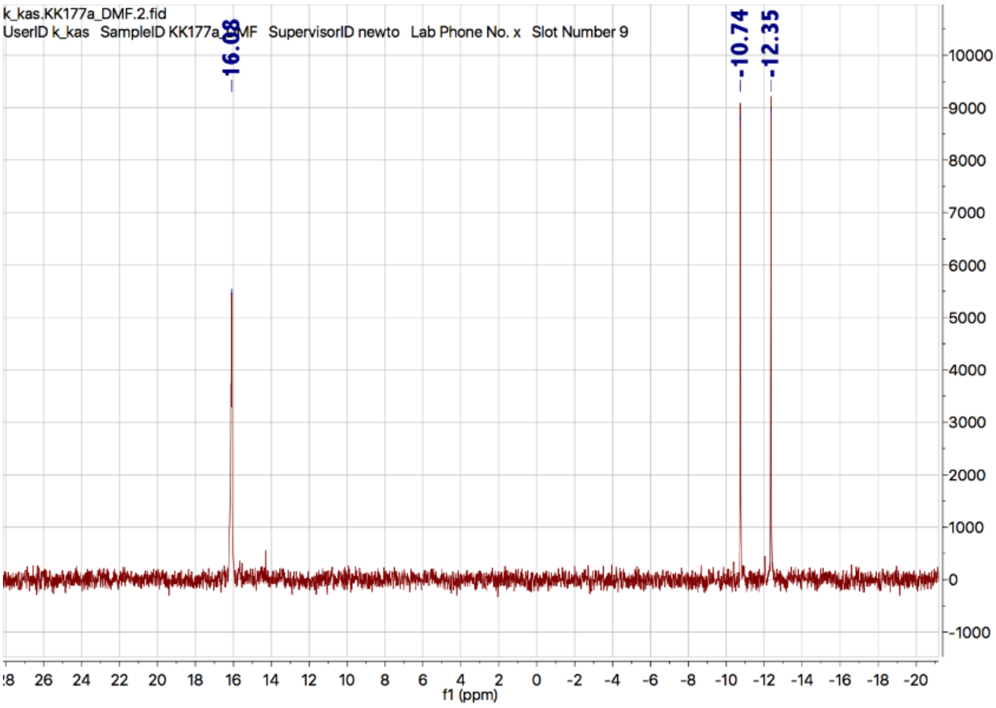

*Figure S4.* $^{31}$*P-NMR of* $H_6$**1** *in DMF-*$d_7$*.*

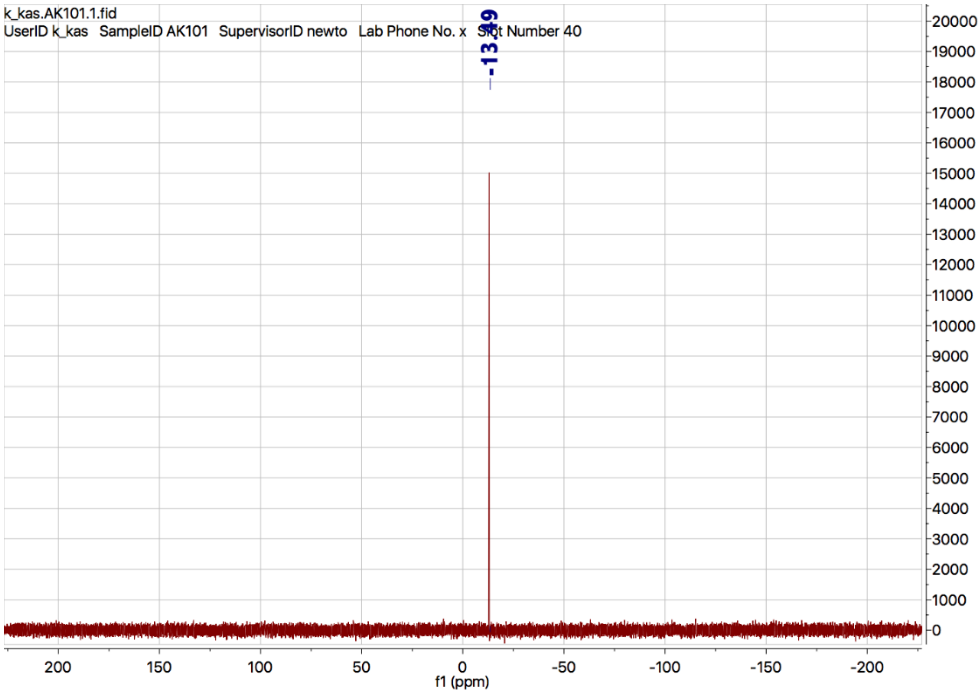

*Figure S5.* $^{31}$*P-NMR of* $\{P_2W_{18}\}$ *in* $D_2O$*.*

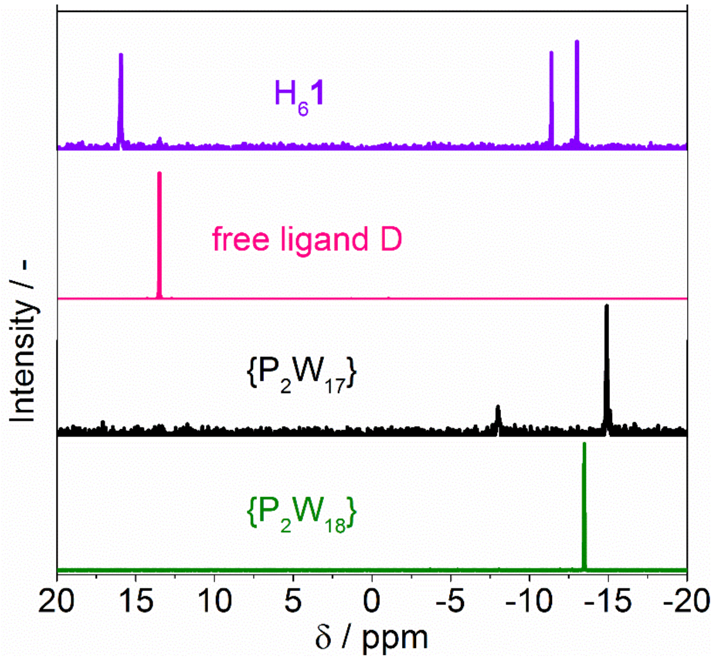

*Figure S6. Comparison of the $^{31}$P-NMR spectra in DMSO-d$_6$ of of H$_6$**1** (violet)**,** the organophosphonate ligand **D** (pink), the non-functionalised lacunary parent-anion [$P_2W_{17}O_{61}$]$^{10-}$ = {$P_2W_{17}$} (black) and the polyoxometalate precursor [$P_2W_{18}O_{62}$]$^{6-}$ = {$P_2W_{18}$} (green) in DMSO-d$_6$.*

## 5. Absorption Spectroscopy

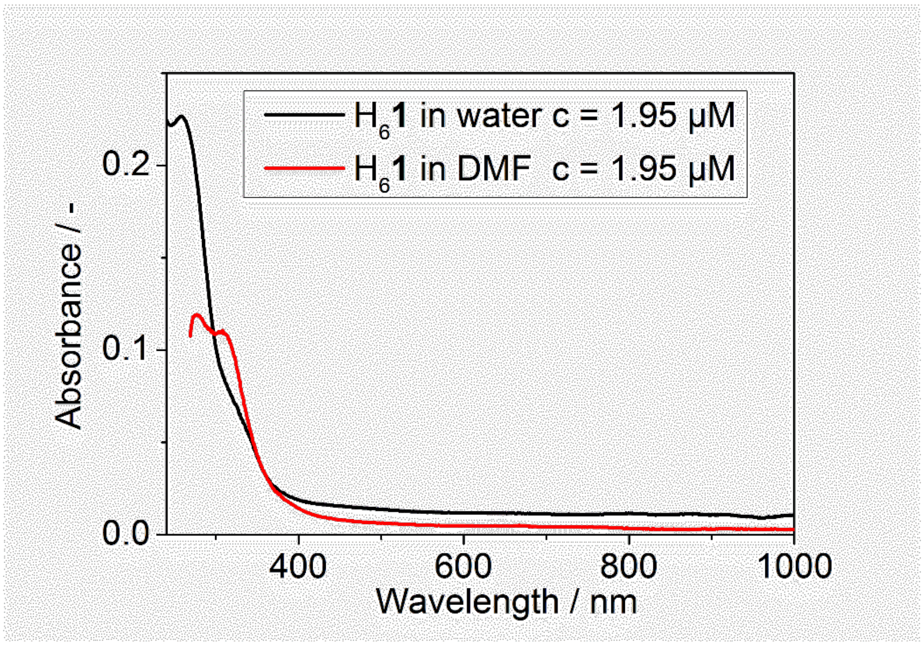

*Figure S7. Comparison of the UV-vis spectra of $H_6$**1** in water and DMF at the same concentration (c = 1.95 µM).*

## 6. Solvatochromism:

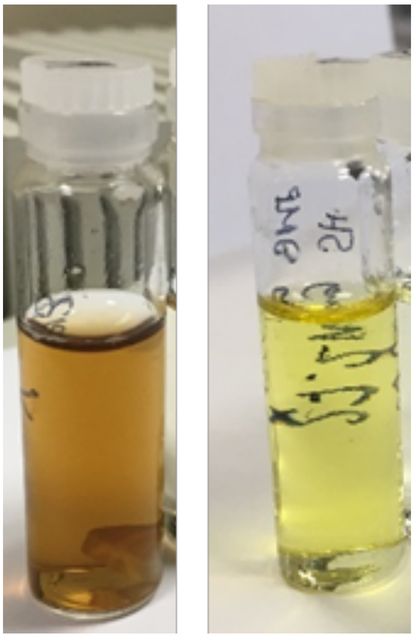

*Figure S8. Photographs of $H_6$**1** in water (left) and DMF (right). Both samples were prepared to the same concentration c = 1.95 mM.*

## 7. TEM of $H_6$**1** in DMF

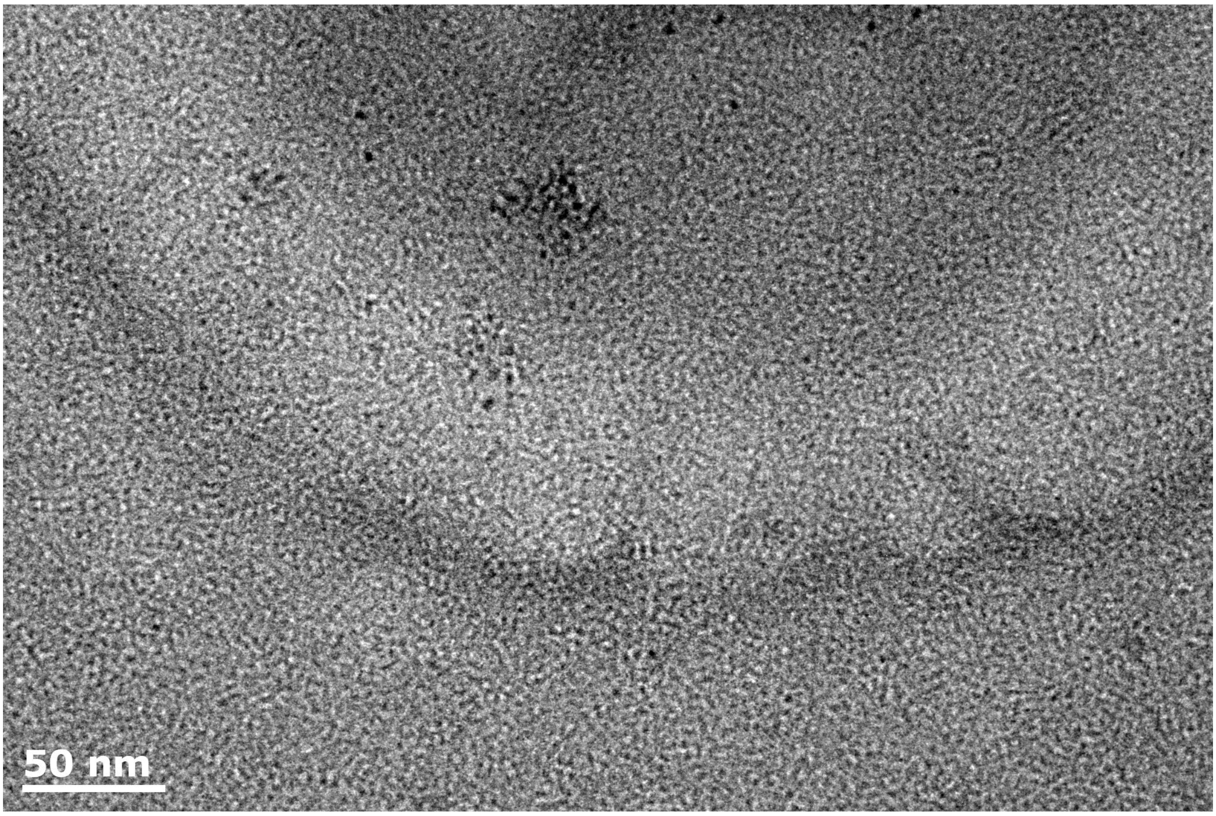

*Figure S9 TEM of $H_6$**1** in DMF*

## 8. Mass-Spectrometry

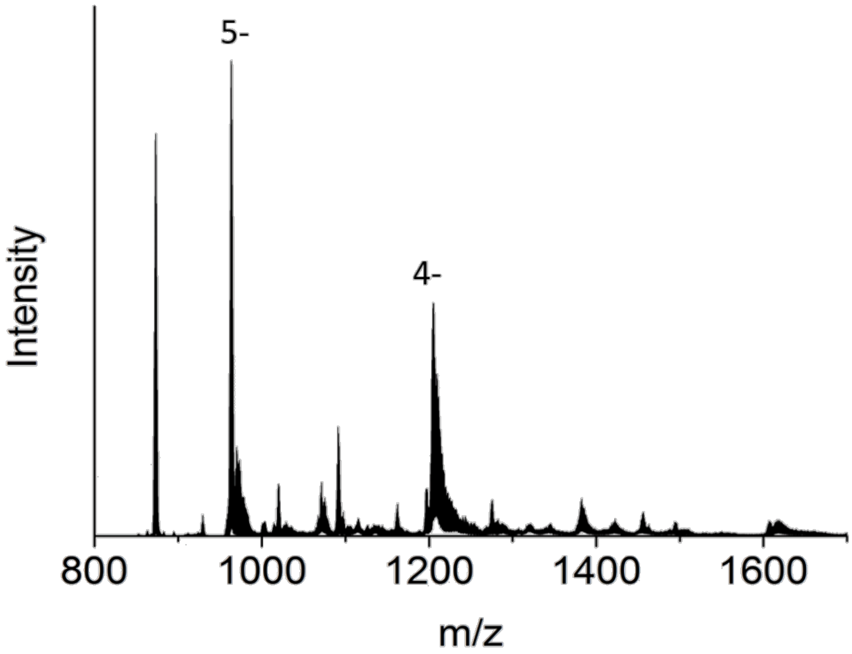

*Figure S10 : Negative mode high resolution ESI mass spectrum of $H_6$**1** in acetonitrile.*

| m/z (obs.) | z | Assignment | m/z (calc.) |
|---|---|---|---|
| 963.8 | 5- | $H_3[P_2W^{VI}{}_{15}W^{V}{}_2O_{61}(PO_2C_{17}H_{26}SH)_2]$ | 963.8 |
| **1204.6** | **4-** | $H_2[P_2W^{VI}{}_{15}W^{V}{}_2O_{61}(PO_2C_{17}H_{26}SH)_2]$ | **1204.5** |

# 9. Thermogravimetric Analysis:

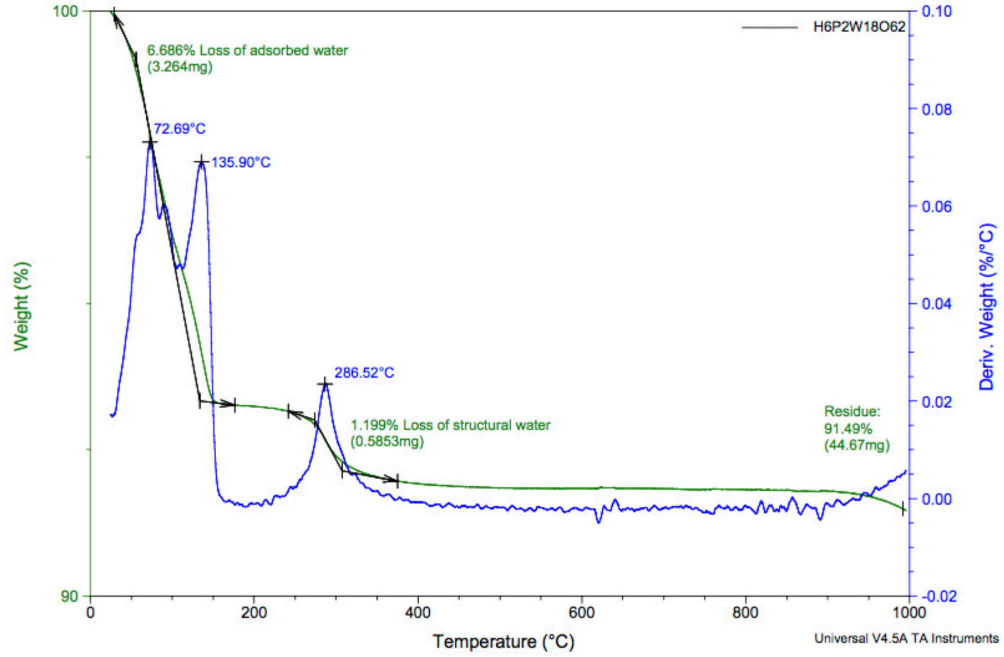

*Figure S11 Thermogravimetric analysis of the polyoxometalate precursor $H_6[P_2W_{18}O_{62}]$.*

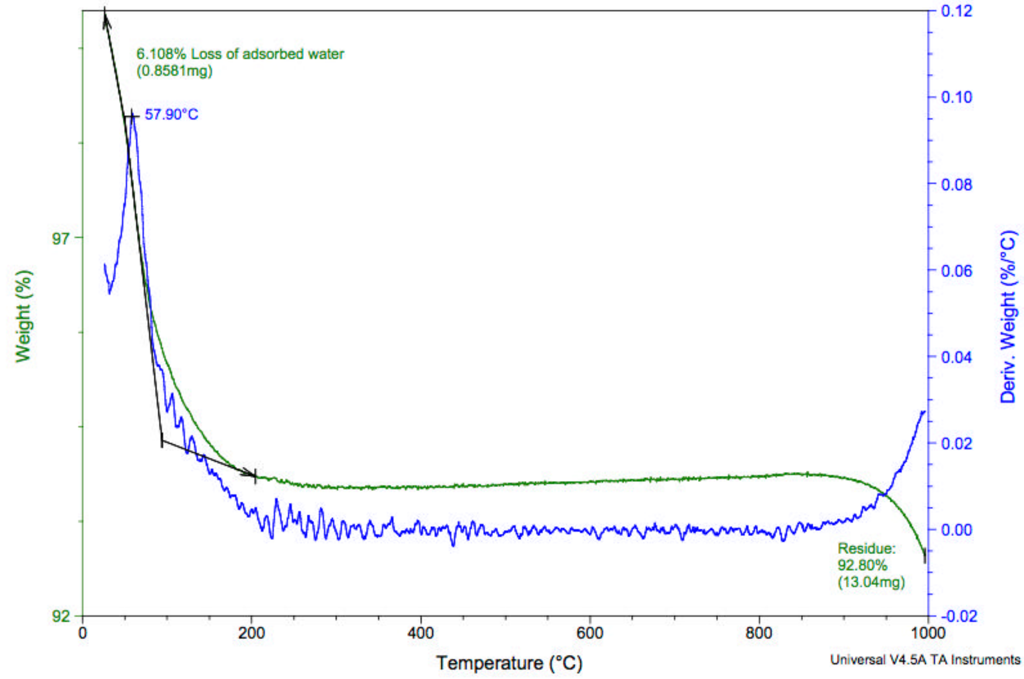

*Figure S12 Thermogravimetric analysis of the non-functionalised lacunary precursor-anion $K_{10}[P_2W_{17}O_{61}]$.*

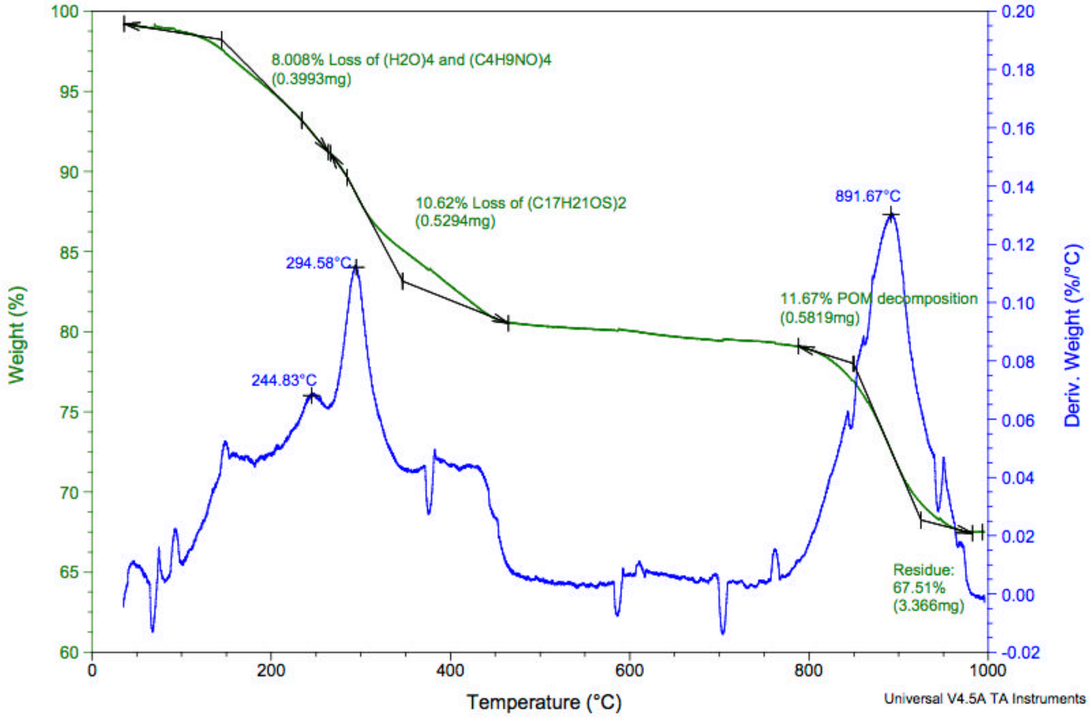

*Figure S13. Thermogravimetric analysis of $H_6$**1**, indicating a weight loss step (25-450°C) corresponding to four water and four dimethylacetamide (= $C_4H_9NO$) solvent molecules and the two organic ligand moieties (= $C_{17}H_{27}OS$) (cleaved at the phosphonate linker unit) of $H_6$**1** (observed: 18.6 wt.-%; calc: 18.7 wt.-%).*

# 10. Electrochemistry and DLS

Cyclic voltammetry (CV) experiments under non-aqueous conditions were performed using a CHI Instruments electrochemical workstation equipped with a standard three-electrode arrangement; working electrode: glassy carbon (d = 1.6 mm), reference electrode: Ag-wire in frit (filled with TBA·$PF_6$ (0.1M) in DMF ), and counter electrode: Pt wire. All potentials with Ferrocene as internal reference are quoted relative to NHE. CV experiments were performed in TBA·$PF_6$ (0.1 M) as supporting electrolyte in dry DMF. All solutions were purged with nitrogen for at least 10 min to remove $O_2$ and kept under a positive pressure of $N_2$ while performing the experiment. Measurements were performed at a scan rate of 100 mV $s^{-1}$.

Cyclic voltammetry (CV) experiments under aqueous conditions and addition of DMF were performed using a CHI Instruments electrochemical workstation equipped with a standard three-electrode arrangement; working electrode: glassy carbon (d = 3 mm), reference electrode:Ag/AgCl (3.5 M), and counter electrode: Pt wire. After the addition of DMF to water, ferrocene was also added as an internal standard. All potentials are quoted relative to NHE. CV experiments were performed in diluted $H_2SO_4$ (0.1 M) as supporting electrolyte. All solutions were purged with nitrogen for at least 10 min to remove $O_2$ and kept under a positive pressure of $N_2$ while performing the experiment. Measurements were performed at a scan rate of 100 mV $s^{-1}$.

Spectroelectrochemical experiments were performed using a CHI Instruments electrochemical workstation equipped with a three-electrode arrangement; working electrode: carbon felt, reference electrode: Ag/AgCl (3.5 M) and counter electrode: Pt wire. A constant potential was applied and current was recorded over time. The change of absorption of the sample during coulometry was recorded with a transmission dip probe (Ocean Optics) connected to a deuterium halogen light source (Ocean Optics, DH-2000) and a spectrometer (Avantes).

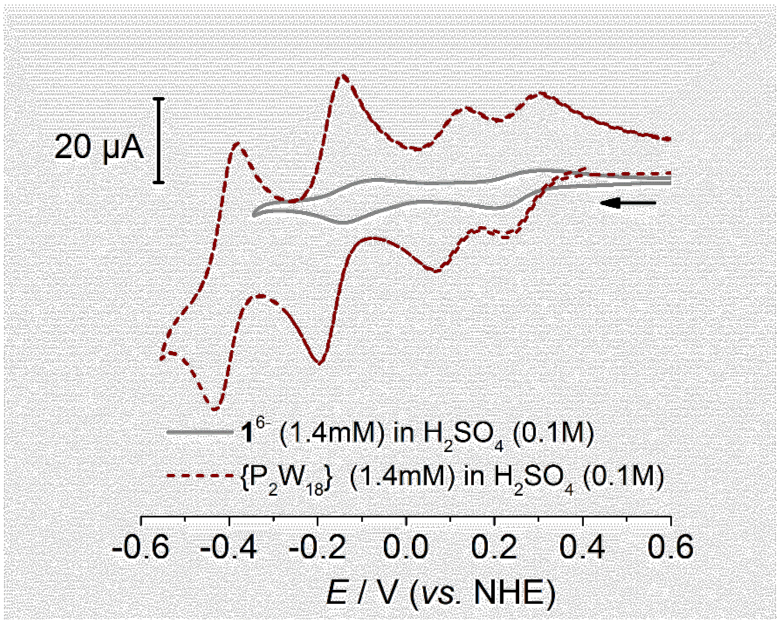

*Figure S14 Comparison of the cyclic voltammograms of $H_6$**1** (1.4 mM) and $K_6P_2W_{18}O_{62}$ = {$P_2W_{18}$} (1.4 mM) recorded in $H_2SO_4$ (0.1M) as supporting electrolyte. Scan rate: 0.1 V/s.*

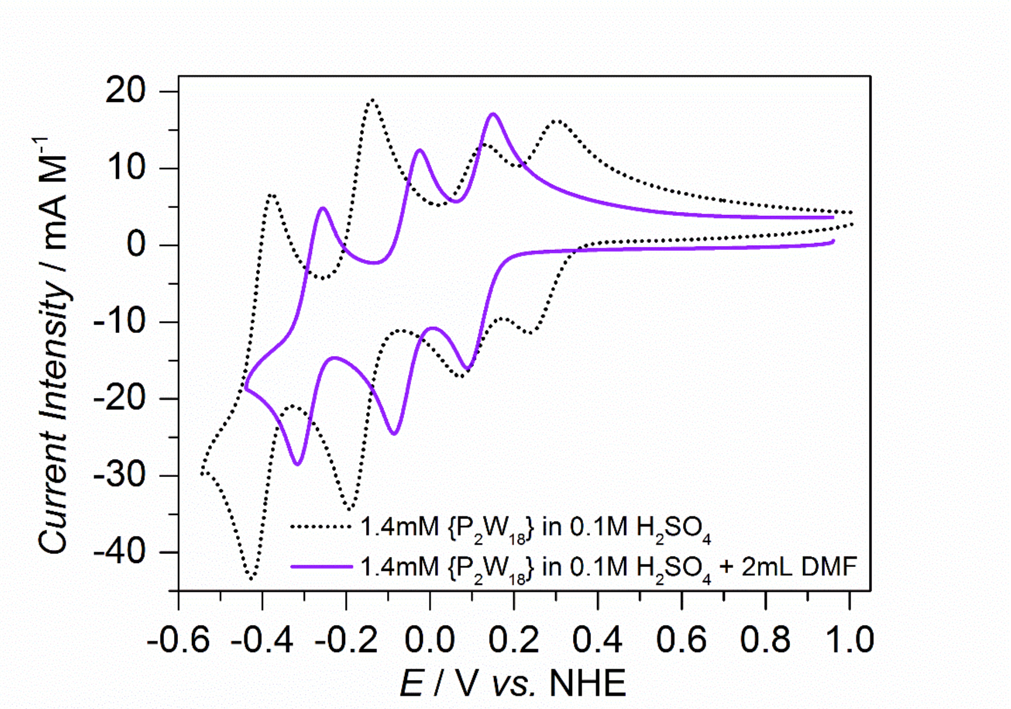

*Figure S15 Comparison of the cyclic voltammograms of {$P_2W_{18}$} (1.4 mM) recorded in $H_2SO_4$ (0.1M) as supporting electrolyte and {$P_2W_{18}$} (c = 1.4 mM) in $H_2SO_4$ (0.1M) after the addition of 2 mL DMF ($c_{new}$ = 0.7 mM). Scan rate: 0.1 V/s.*

DLS measurements were conducted on a solution of $H_6$**1** (1.4 mM) in 0.1M $H_2SO_4$, matching the conditions used in the electrochemical analysis (Figure 2C and Figure S9).

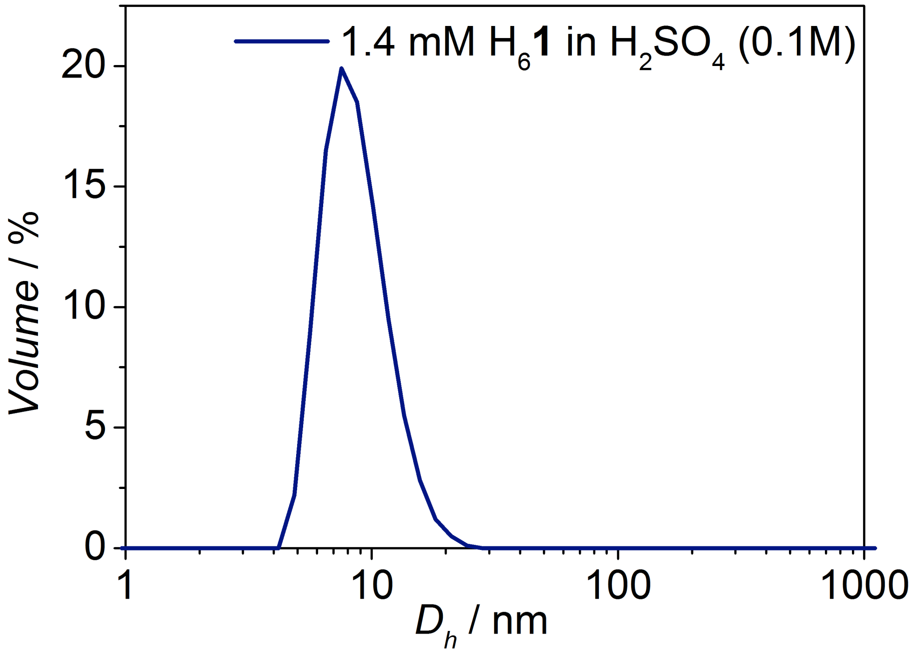

*Figure S16 Particle-size distribution curves determined by DLS of $H_6$**1** (1.4 mM) in 0.1M $H_2SO_4$.*

Further DLS measurements were performed on a solution of $H_6$**1** (0.5 mM) in 0.1M $H_2SO_4$ before and after the reduction of the sample by 2 electrons and after re-oxidation.

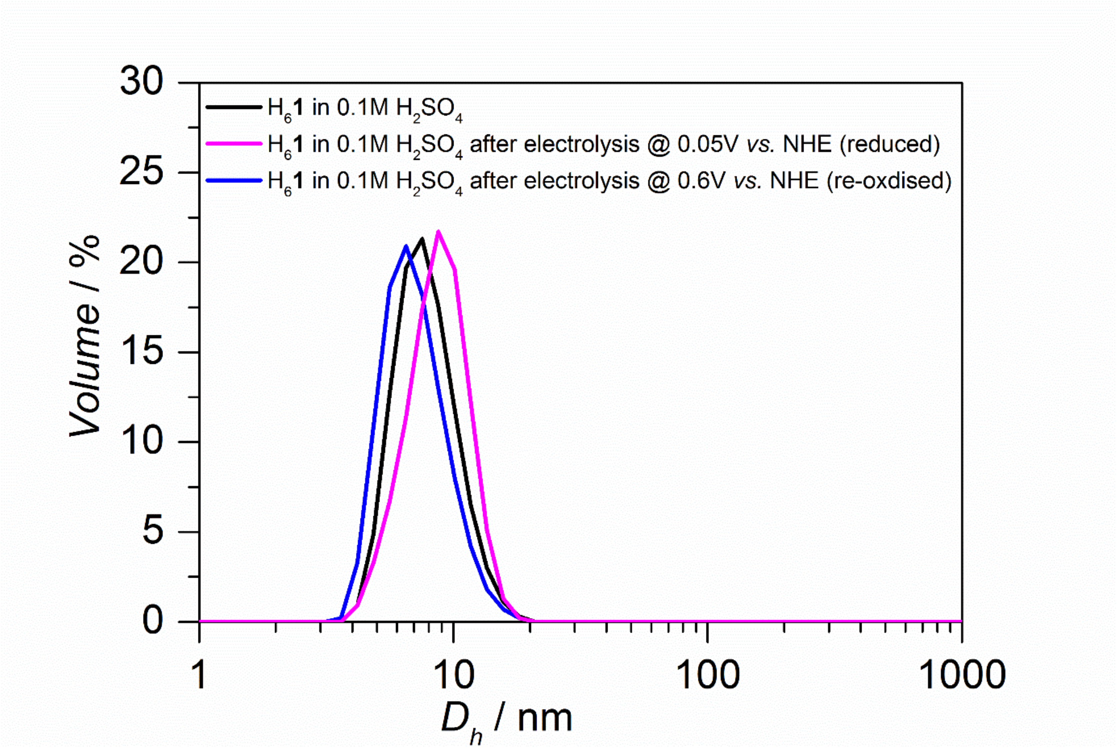

*Figure S17 Particle-size distribution curves determined by DLS of $H_6$**1** (0.5 mM) in 0.1M $H_2SO_4$ before and after electrolysis at 0.05V (= sample reduced by 2 electrons) and 0.6V (=sample re-oxidised by 2 electrons), both vs. NHE. $D_h$ maxima at 7.4 nm (black), 8.6 nm (pink) and 6.7 nm (blue).*

## 11. $^1$H-NMR Experiment: Addition of DMF-$d_7$ to a solution of $H_6$**1** in $D_2O$:

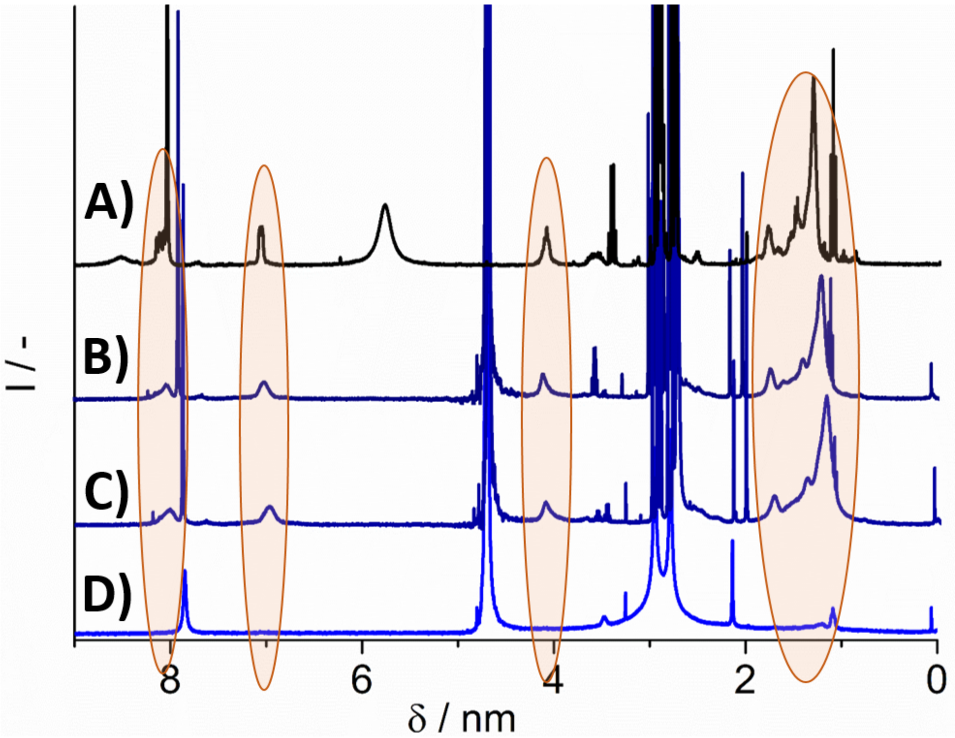

*Figure S18 Study of the proton signals in the $^1$H-NMR spectra of $H_6$**1** in pure DMF-$d_7$ (**A**) and pure $D_2O$ (**D**). In water, the $^1$H-NMR of $H_6$**1** does not show any signals for the organic ligands (highlighted in red) while $H_6$**1** in DMF shows all ligand based signals. Upon addition of portions of DMF to the sample **D** (to give solvent ratios of DMF/water (v:v = 1:5, **B** and v:v = 1:5, **C**)) the ligand based signals appear in the $^1$H-NMR spectra (highlighted areas).*

## 12. References

[1] R. Contant, Inorganic Syntheses; John Wiley & Sons, 1990; Vol. 27, 107.